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(54) Fluorosilicone composition and its gellike cured product

Fluorosilikonzusammensetzung und gehärtetes gelartiges Produkt

Composition de fluorosilicone et produit durci du type gel

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EP-A- 0 208 239 EP-A- 0 279 706
EP-A- 0 488 709

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Description

BACKGROUND OF THE INVENTION5 1. Field of the Invention

The present invention relates to a gellike cured product that is excellent in chemical resistance and is obtained from an addition reaction curable fluorosilicone composition.

10 2. Description of the Prior Art

It is known that since addition curable fluorosilicone compositions using as a base polymer an organopolysiloxane with 3,3,3-trifluoropropyl groups can form a gellike cured product excellent in properties such as gasoline resistance and oil resistance, they are useful for parts for aircraft.

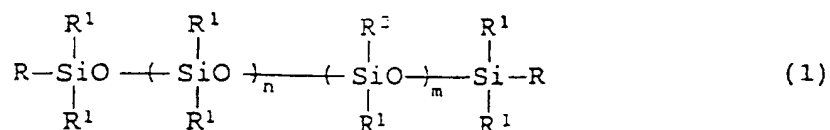
15 However, the above fluorosilicone compositions are still unsatisfactory in chemical resistance such as acid resistance and further improvement is required.

SUMMARY OF THE INVENTION

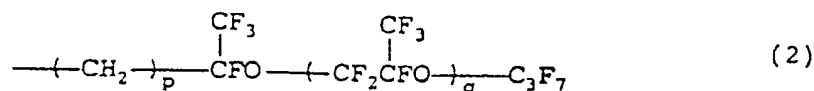
20 Therefore, an object of the present invention is to provide, from an addition curable fluorosilicone composition, a gel cured product remarkably improved in chemical resistance such as acid resistance.

According to the present invention, there is provided a silicone gel having a penetration of 0 to 200 when measured according to ASTM D-1403 (¼ Scale Cone), obtained by curing a fluorosilicone composition comprising:

25 (A) an alkenyl group-containing organopolysiloxane represented by the following general formula (1):

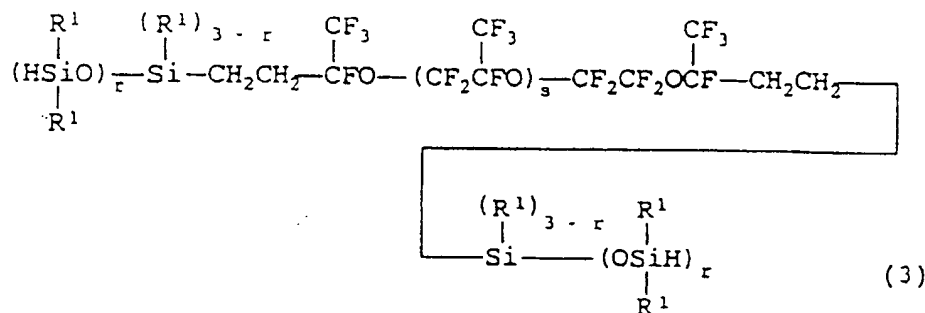


35 wherein R represents an alkenyl group, R¹'s, which may be the same or different, each represent an alkyl group having 1 to 8 carbon atoms or a phenyl group, R² represents a group represented by the following formula (2)



in which p is an integer of 2 to 8 and q is an integer of 1 to 10, and n and m are each a positive integer,

45 (B) a hydrosiloxane having silicon-bonded hydrogen atoms represented by the following general formula (3):



wherein R¹ has the same meaning as defined above, r is an integer of 2 or 3, and s is a positive integer, and (C) a platinum family metal catalyst, wherein said hydrosiloxane (B) is present in such an amount that the SiH groups contained in said hydrosiloxane (B) amount to 0.1 to 1 mol per mol of the alkenyl groups in said component (A).

Herein, the term "gellike cured product" means a product which has partially a three-dimensional network, is deformed or fluidized when stressed, and has a penetration of 0 to 200 measured according to ASTM D-1403 (¼ Scale Cone), suitably a penetration in the range 85 to 200.

Fluorosilicone compositions similar to those used herein are described in our earlier Specification No. EP-A-0488709.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

(A) Organopolysiloxanes

The component (A) of the fluorosilicone composition is represented by the above general formula (1) and is a linear fluorine-containing organopolysiloxane with alkenyl groups at both ends of the chain of the molecule.

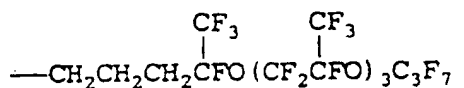
In the general formula (1), R represents an alkenyl group, which preferably has 2 to 8 carbon atoms and specific examples include a vinyl group, an allyl group, a 1-butenyl group, and a 1-hexenyl group.

R¹ is selected from the group consisting of an alkyl group having 1 to 8 carbon atoms such as a methyl group, an ethyl group, a butyl group, a hexyl group, a cyclohexyl group, and an octyl group, and a phenyl group.

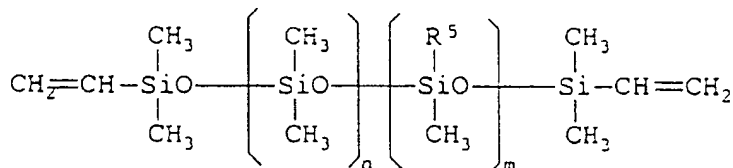
The group R² represented by the above formula (2) has a structure wherein an oligomer of hexafluoropropylene oxide is bonded to an alkylene group and is quite important to improvement in chemical resistance of the gellike cured product. Preferable examples of R² include the following, which do not restrict the present invention.

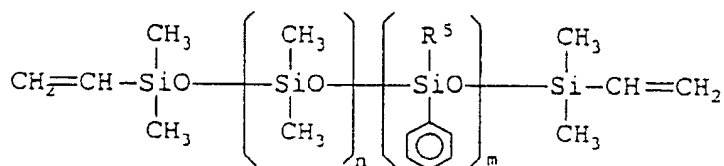
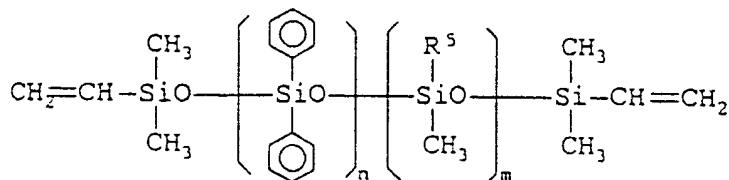
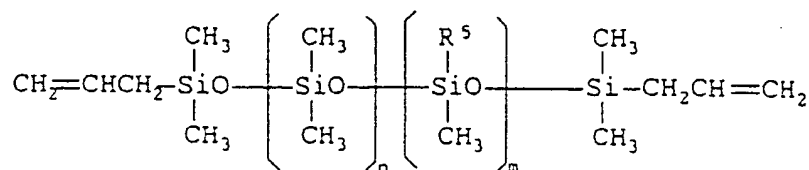


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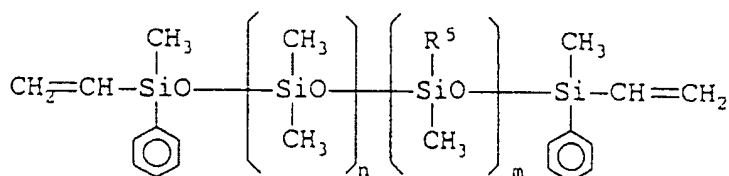


In the present invention, typical examples of the component (A) which is an alkenyl group-containing organopolysiloxane represented by the above-mentioned general group (1) include the following:

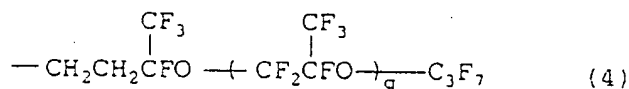




and



wherein R^5 represents a fluorine-containing group represented by the following formula (4):



in which q is an integer of 1 to 10, preferably 1 to 5, and n and m are each a positive integer, preferably a number such that $m/(n+m)$ is 0.1 or more but less than 1.

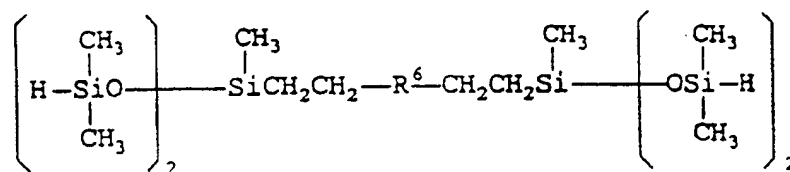
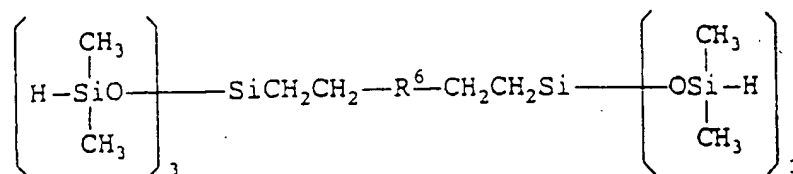
This organopolysiloxane has preferably a viscosity at 25°C in the range of 50 to 10,000 mPa.s, particularly 100 to 1,000 mPa.s, in order to give the composition a suitable fluidity before the curing and to give to the cured composition (gellike cured product) suitable adhesiveness and suitable physical properties.

The above-mentioned organopolysiloxane, the component (A), can be produced, for example, by a process disclosed in Japanese Pre-examination Patent Publication (kokai) No. 4-25563 (1992).

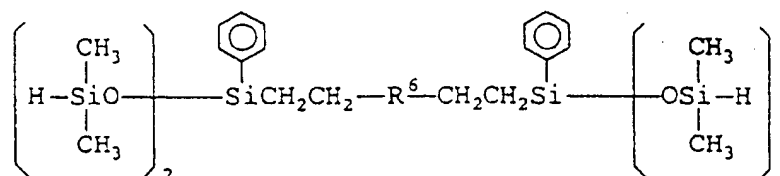
(B) Hydrogensiloxanes

The component (B) of the fluorosilicone composition is represented by the above formula (3) and is a fluorine-containing organosiloxane having silicon-bonded hydrogen atoms at the ends of the molecule.

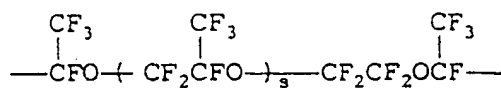
Examples of the hydrogensiloxane, the component (B), include the following compounds:



and



wherein R^6 represents a bivalent fluorine-containing group represented by the following formula:



in which s is a positive integer, preferably an integer of 1 to 10.

When the SiH groups in the hydrogensiloxane undergoes an addition reaction with the alkenyl groups in the component (A), a gellike cured product (silicone gel) is formed. For the formation of a silicone gel, the hydrogensiloxane is used in such an amount that the SiH groups thereof amount to 0.1 to 1 mol per mol of the alkenyl groups in the component (A).

This hydrogensiloxane can be produced, for example, by a process disclosed in Japanese Pre-examination Patent Publication (kokai) No. 3-251589 (1991).

(C) Platinum family metal catalysts

The platinum family metal catalyst, the component (C) of the fluorosilicone composition, is a known catalyst for subjecting the alkenyl groups in the component (A) and the silicon-bonded hydrogen atoms (SiH groups) in the component (B) to an addition reaction and serves as a curing accelerator.

Such a catalyst includes a platinum catalyst, a palladium catalyst, and a rhodium catalyst, and the platinum catalyst includes, for example, chloroplatinic acid, a solution of chloroplatinic acid modified with an alcohol, a coordination compound of chloroplatinic acid with an olefin or a vinyl siloxane, the palladium catalyst includes, for example, tetrakis

(triphenylphosphine)palladium, and the rhodium catalyst includes, for example, chlorotris (triphenylphosphine)rhodium, with preference given to the platinum catalyst.

The amount of the platinum family metal catalyst, the component (C), to be used is generally in the range of 0.1 to 100 ppm in terms of the platinum family metal based on the total amount of the component (A) and the component (B).

Other components

In the fluorosilicone composition, besides the above components (A) to (C), various ingredients which are known per se can be added if necessary.

The hardness and mechanical strength of the gellike cured product obtainable from the fluorosilicone composition can be adjusted by adding, for example, an inorganic filler such as fumed silica, silica aerosil, precipitated silica, ground silica, diatomaceous earth, iron oxide, zinc oxide, titanium oxide, calcium carbonate, magnesium carbonate, zinc carbonate, and carbon black. Indeed, a hollow inorganic filler, a hollow organic filler, an organosilicone resin or rubberlike spherical filler and the like can also be added. Further, a reaction retarding agent such as a polymethylvinylsiloxane cyclic compound, an acetylene compound, and an organophosphorus compound can be added to control the curing reaction. The amount of these ingredients to be added is arbitrary unless the properties of the gellike cured product are not impaired.

Formation of the gellike cured product

By curing the fluorosilicone composition comprising the above-mentioned components, a gellike cured product excellent in chemical resistance can be formed.

The formation of a gellike cured product is carried out in a conventional known manner, for example, by pouring the present addition reaction curable fluorosilicone composition into a suitable mold, where the curing is effected, or coating the composition on a suitable substrate and then curing the composition. The curing can be effected easily by heat treatment generally at a temperature of 60 to 150°C for about 30 to 80 min.

Uses

Because the gellike cured product of the present invention is excellent in electrical insulating properties, stability in electrical properties, and flexibility, the gellike cured product is used as a material for encapsulating or potting electrical or electronic parts. Particularly, the gellike cured product is used in covering control circuit elements such as power transistors, IC, and condensers to protect them from thermal and mechanical failures.

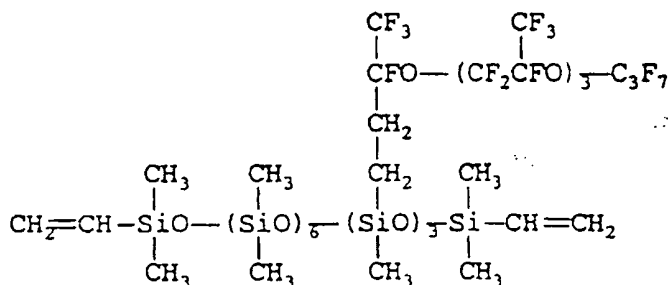
Further, since the gellike cured product of the present invention is particularly excellent in chemical resistance, where the gellike cured product is used for electrical or electric parts to be mounted on automobiles, these parts can be protected from gasoline, and NO_x, SO_x, etc. in exhaust gas.

EXAMPLES

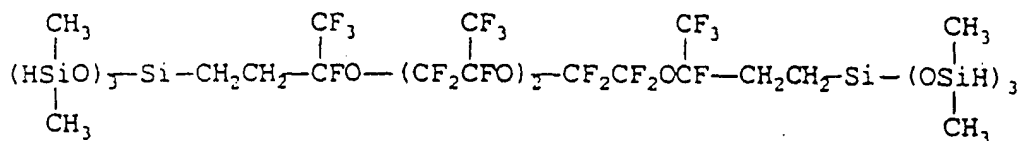
The present invention will now be described with reference to the following Examples. In the following Examples and Comparative Example, the values of viscosities are all measured at 25°C.

Example 1

100 parts by weight of an organopolysiloxane (viscosity: 700 mPa.s) represented by the following formula:



4 parts by weight of a hydrogensiloxane (viscosity: 15 mPa.s) represented by the following formula:



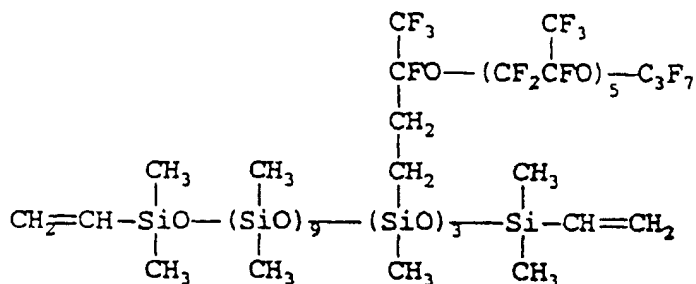
and 0.02 part by weight of a complex of tetramethyldivinylidisiloxane with chloroplatinic acid (Pt: 3 % by weight) were mixed uniformly to prepare Composition I.

Composition I was heated at 150°C for 1 hour to obtain a transparent gellike cured product. The penetration of the cured produce was measured (ASTM D-1403; 1/4 Scale Cone). The result is shown in Table 1.

Further, Composition I was applied to a square aluminum piece measuring 1 cm x 1 cm in a glass Petri dish to form a coating with a thickness of 1 mm and then the piece was immersed in a hydrochloric acid solution (pH: 1) at 50°C to carry out an acid resistance test. The time required until the aluminum piece is eroded shown in Table 1.

Example 2

Example 1 was repeated, except that, in place of the organopolysiloxane used in Example 1, an organopolysiloxane (viscosity: 800 mPa.s) represented by the following formula:

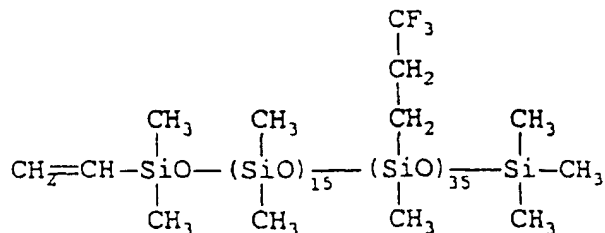


was used, thereby preparing Composition II.

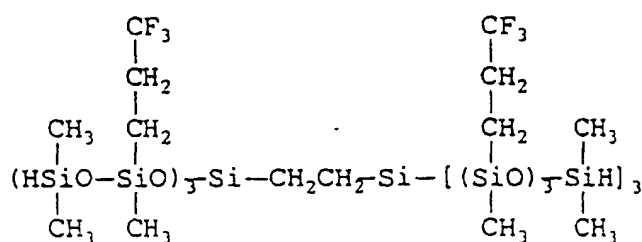
With respect to Composition II, the measurement of the penetration and the acid resistance test were carried out in the same way as in Example 1. The results are shown in Table 1.

Comparative Example 1

100 parts by weight of an organopolysiloxane (viscosity: 700 mPa.s) represented by the following formula:



15 parts by weight of a hydrogensiloxane (viscosity: 130 cP) represented by the following formula:



and 0.02 part by weight of a complex of tetramethyldivinylidisiloxane with chloroplatinic acid (Pt: 3 % by weight) were mixed uniformly to prepare Composition III.

With respect to Composition III, similarly to Example I, the measurement of the penetration and the acid resistance test were carried out. The results are shown in Table 1.

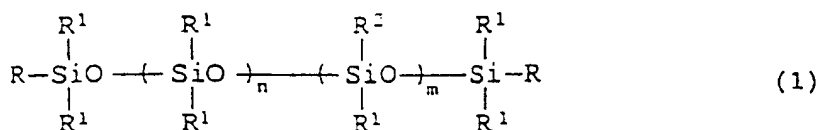
TABLE 1

	Example 1	Example 2	Comparative Example 1
Penetration	85	90	65
Acid resistance	600 hr.	800 hr.	300 hr.

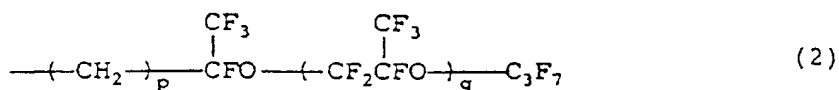
Claims

1. A silicone gel having a penetration of 0 to 200 when measured according to ASTM D-1403 (¼ Scale Cone), obtained by curing a fluorosilicone composition comprising:

(A) an alkenyl group-containing organopolysiloxane represented by the following general formula (1):

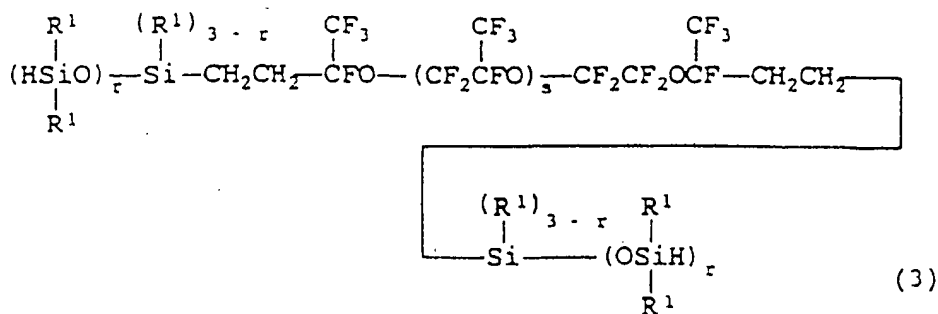


wherein R represents an alkenyl group, R¹'s, which may be the same or different, each represent an alkyl group having 1 to 8 carbon atoms or a phenyl group, R² represents a group represented by the following formula (2)



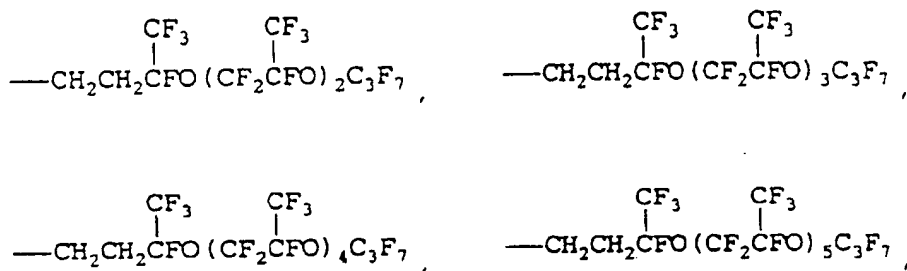
in which p is an integer of 2 to 8 and q is an integer of 1 to 10, and n and m are each a positive integer,

(B) a hydrogensiloxane having silicon-bonded hydrogen atoms represented by the following general formula (3):

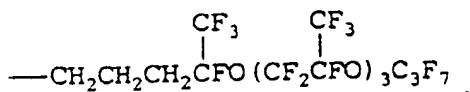


wherein R^1 has the same meaning as defined above, r is an integer of 2 or 3, and s is a positive integer, and (C) a platinum family metal catalyst, wherein said hydrogensiloxane (B) is present in such an amount that the SiH groups contained in said hydrogensiloxane (B) amount to 0.1 to 1 mol per mol of the alkenyl groups in said component (A).

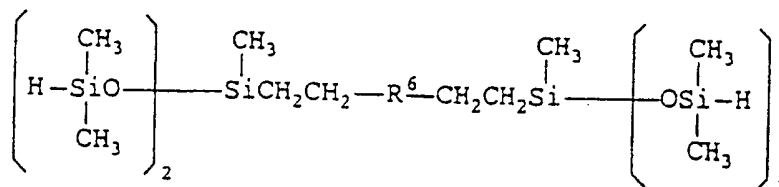
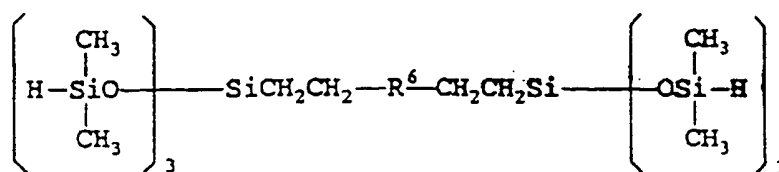
2. A silicone gel as claimed in claim 1, wherein said alkenyl group-containing organopolysiloxane (A) is an alkenyl group-containing organopolysiloxane of said general formula (1) wherein R represents a vinyl group and R^1 represents a methyl group or a phenyl group.
3. A silicone gel as claimed in claim 1, wherein said alkenyl group-containing organopolysiloxane (A) is an alkenyl group-containing organopolysiloxane of said general formula (1) wherein n and m are positive integers such that $m/(n+m)$ is 0.1 or more but less than 1.
4. A silicone gel as claimed in claim 1, wherein said alkenyl group-containing organopolysiloxane (A) is an alkenyl group-containing organopolysiloxane wherein, in the general formula (1), R^2 is a group selected from the group consisting of



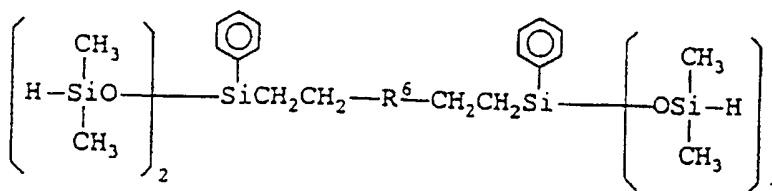
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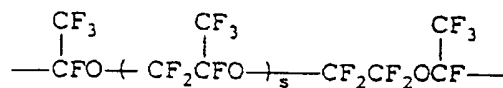
5. A silicone gel as claimed in claim 1, wherein said hydrogensiloxane (B) is at least one compound selected from the group consisting of compounds represented by the following formulas



and



wherein R^6 represents a bivalent fluorine-containing group represented by the following formula:



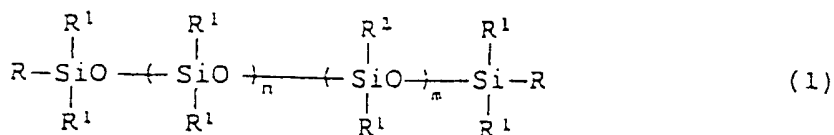
in which s is a positive integer.

6. A silicone gel as claimed in claim 1 wherein the penetration is in the range 85 to 200.

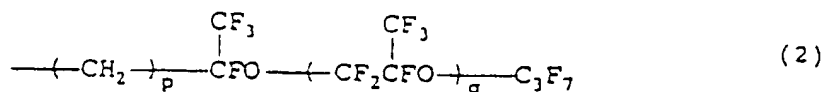
Patentansprüche

1. Silicongel mit einer Penetration von 0 bis 200, gemessen gemäß ASTM D-1403 (¼ Scale Cone), erhalten durch Härten einer Fluorsiliconmasse, umfassend:

(A) ein Alkenylgruppe-enhaltendes Organopolysiloxan, wiedergegeben durch die nachstehende allgemeine Formel (1):

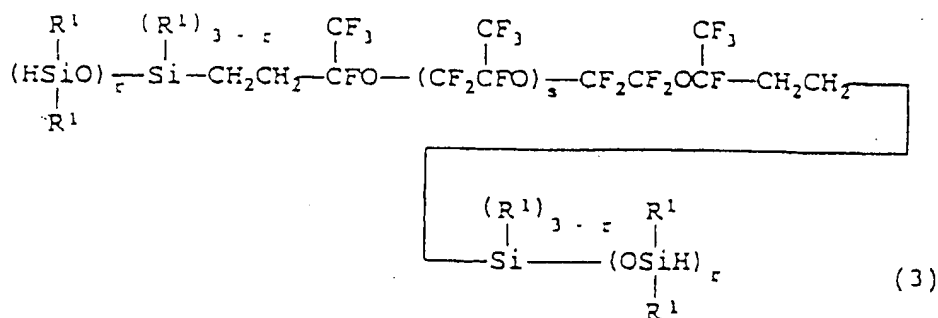


worin R eine Alkenylgruppe wiedergibt, die Reste R¹, die gleich oder verschieden sein können, jeweils eine Alkylgruppe mit 1 bis 8 Kohlenstoffatomen oder eine Phenylgruppe wiedergeben, R² eine Gruppe, wiedergegeben durch die nachstehende Formel (2),



in der p eine ganze Zahl von 2 bis 8 ist und q eine ganze Zahl von 1 bis 10 ist und n und m jeweils eine positive ganze Zahl sind, wiedergibt,

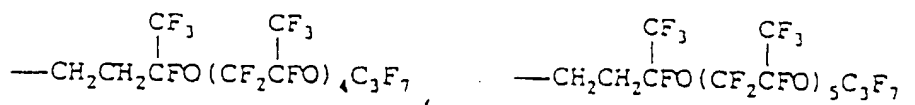
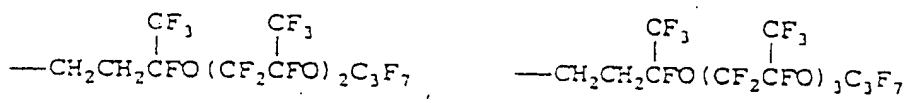
(B) ein Hydrogensiloxan mit Silicium-gebundenen Wasserstoffatomen, wiedergegeben durch die nachstehende allgemeine Formel (3):



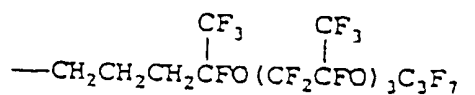
worin R¹ die gleiche wie vorstehend definierte Bedeutung aufweist, r eine ganze Zahl von 2 oder 3 ist und s eine positive ganze Zahl ist, und

(C) einen Katalysator eines Metalls der Platinfamilie, wobei das Hydrogensiloxan (B) in einer solchen Menge vorliegt, daß die Gruppen SiH in dem Hydrogensiloxan (B) in einer Menge von 0,1 bis 1 Mol pro Mol der Alkenylgruppen in der Komponente (A) enthalten sind.

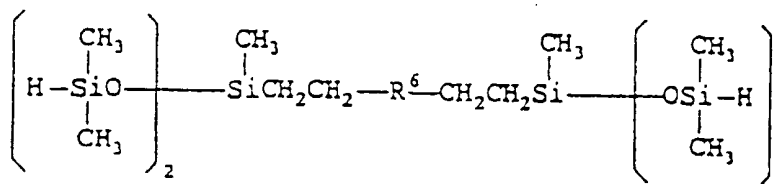
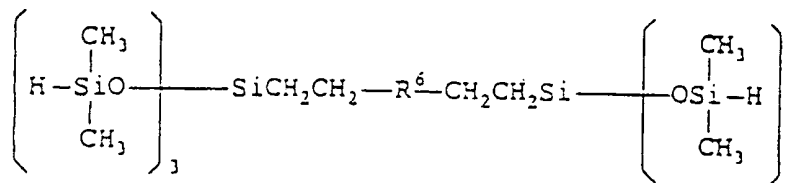
2. Silicongel nach Anspruch 1, wobei das Alkenylgruppe-enthaltende Organopolysiloxan (A) ein Alkenylgruppe-enthaltendes Organopolysiloxan der allgemeinen Formel (1) darstellt, worin R eine Vinylgruppe wiedergibt und R¹ eine Methylgruppe oder eine Phenylgruppe wiedergibt.
3. Silicongel nach Anspruch 1, wobei das Alkenylgruppe-enthaltende Organopolysiloxan (A) ein Alkenylgruppe-enthaltendes Organopolysiloxan der allgemeinen Formel (1) ist, worin n und m positive ganze Zahlen sind, so daß m/(n+m) 0,1 oder mehr ist, jedoch weniger als 1 ist.
4. Silicongel nach Anspruch 1, wobei das Alkenylgruppe-enthaltende Organopolysiloxan (A) ein Alkenylgruppe-enthaltendes Organopolysiloxan darstellt, worin in der allgemeinen Formel (1) R² eine Gruppe darstellt, ausgewählt aus der Gruppe, bestehend aus



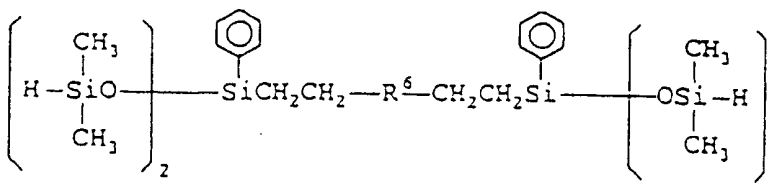
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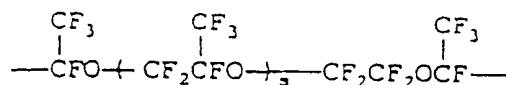
5. Silicongel nach Anspruch 1, wobei das Hydrogensiloxan (B) mindestens eine Verbindung darstellt, ausgewählt aus der Gruppe, bestehend aus Verbindungen, wiedergegeben durch die nachstehenden Formeln



und



worin R⁶ eine zweiwertige Fluor-enthaltende Gruppe darstellt, wiedergegeben durch die allgemeine Formel:



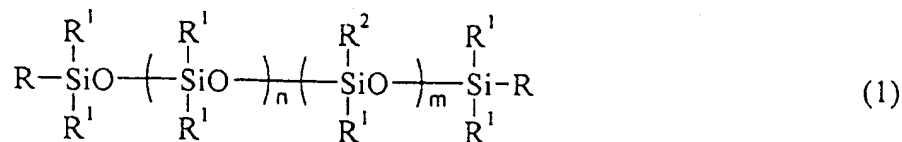
worin s eine positive ganze Zahl darstellt.

6. Silicongel nach Anspruch 1, wobei die Penetration im Bereich 85 bis 200 liegt.

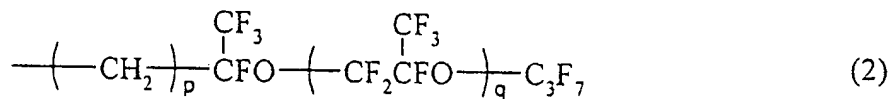
Revendications

1. Gel de silicone ayant une pénétration de 0 à 200 telle que mesurée conformément à la norme ASTM D-1403 (cône à l'échelle ¼), obtenu par durcissement d'une composition de fluorosilicone comprenant :

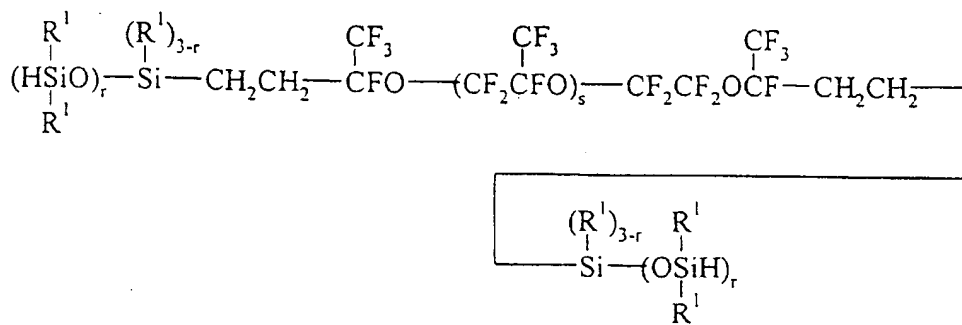
(A) un polyorganosiloxane contenant un groupe alcényle, représenté par la formule générale (1) suivante :



dans laquelle R représente un groupe alcényle, les radicaux R¹, qui peuvent être identiques ou différents, représentent chacun un groupe alkyle ayant de 1 à 8 atomes de carbone ou un groupe phényle, R² représente un groupe représenté par la formule (2) suivante :



dans laquelle p est un entier de 2 à 8 et q est un entier de 1 à 10, et n et m sont chacun un entier positif, (B) un hydrogénosiloxane ayant des atomes d'hydrogène à liaison silicium, représenté par la formule générale (3) suivante :



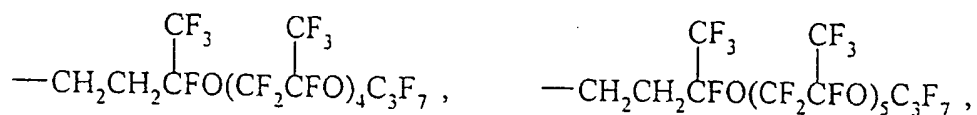
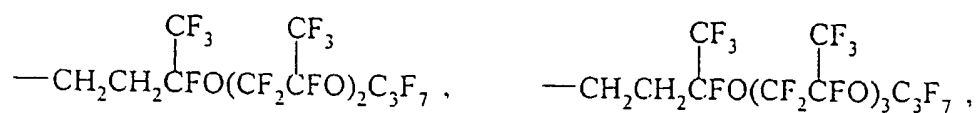
(3)

dans laquelle R¹ a la même signification que celle indiquée ci-dessus, r est un entier valant 2 ou 3, et s est un entier positif, et

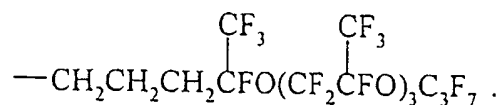
(C) un catalyseur de métal de la famille du platine,

dans lequel ledit hydrogénosiloxane (B) est présent en une quantité telle que les groupes SiH présents dans ledit hydrogénosiloxane (B) représentent de 0,1 à 1 mole par mole des groupes alcényle dans ledit composant (A).

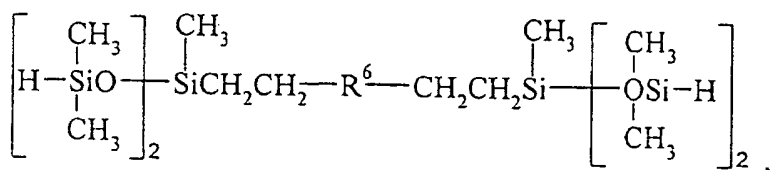
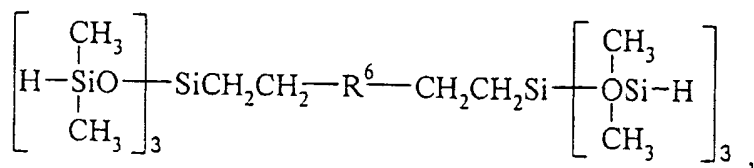
2. Gel de silicone selon la revendication 1, dans lequel ledit polyorganosiloxane contenant un groupe alcényle (A) est un polyorganosiloxane contenant un groupe alcényle de ladite formule générale (1) dans laquelle R représente un groupe vinyle et R¹ représente un groupe méthyle ou un groupe phényle.
3. Gel de silicone selon la revendication 1, dans lequel ledit polyorganosiloxane contenant un groupe alcényle (A) est un polyorganosiloxane contenant un groupe alcényle de ladite formule générale (1) dans laquelle n et m sont des entiers positifs tels que m/(n+m) vaille 0,1 ou plus mais moins de 1.
4. Gel de silicone selon la revendication 1, dans lequel ledit polyorganosiloxane contenant un groupe alcényle (A) est un polyorganosiloxane contenant un groupe alcényle dans lequel, dans la formule générale (1), R² est un groupe choisi dans l'ensemble constitué par :



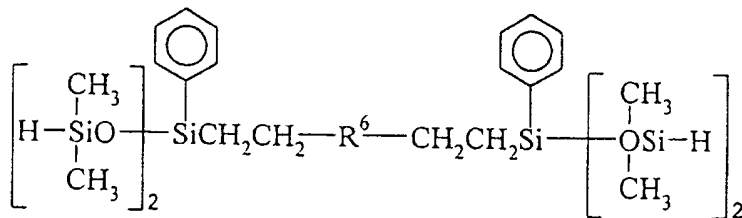
et



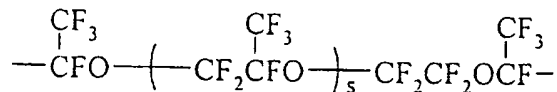
5. Gel de silicone selon la revendication 1, dans lequel ledit hydrogénosiloxane (B) est au moins un composé choisi dans l'ensemble constitué par les composés représentés par les formules suivantes :



et



dans lesquelles R⁶ représente un groupe fluoré bivalent représenté par la formule suivante :



dans laquelle s est un entier positif.

6. Gel de silicone selon la revendication 1, dans lequel la pénétration est située dans l'intervalle allant de 85 à 200.

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